

Exhibit B

Vapor Pressure of Complex Mixtures

By

Hal B. Coats



*A thesis submitted in partial fulfillment of
the requirements for the degree of Doctor
of Philosophy at the University of Michigan.*

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THE VAPOR PRESSURE OF GASOLINE

DEFINITION

Vapor pressure is that pressure exerted by a liquid (or solid) in contact with that vapor with which the liquid (or solid) is in equilibrium. Vapor pressure may also be regarded as the minimum pressure necessary to prevent the formation of the vapor phase, or as the tendency to form vapor.

IMPORTANCE

Vapor pressure has always been recognized as an important property of natural gasolines in indicating shipping hazards, losses in transit and storage, and recently as an indication of the tendency of fuels to vapor-lock in carburetors of motor cars and gasoline lines of airplanes. For the last reason it was necessary in our study of the vapor-lock to thoroughly investigate vapor pressure of motor fuels from all standpoints.

METHODS OF MEASURING VAPOR PRESSURE

CLASSIFICATION

The three common classes of methods for measuring the vapor pressure of a liquid are the dynamic, static, and partial pressure methods.

The *dynamic method* consists in heating the liquid under a definitely maintained pressure until it boils. Under these conditions boiling will continue at a constant temperature which is recorded.

In the *static method* a quantity of the liquid is inserted into a Toricellian vacuum, or a volume filled with liquid is increased causing the formation of vapor, the temperature regulated to a definite value and the pressure read.

The *partial pressure method* assumes the validity of Dalton's law of Partial Pressures. A measured quantity of a gas such as air, or better a gas of one component, is placed in contact with the liquid previously saturated with this gas, the whole system maintained at a constant temperature and pressure. After equilibrium is established, the gas phase is usually removed and measured, preferably under the same conditions of temperature and pressure as the original gas sample. From the two gas volumes and the total pressure on the gas-liquid system, the vapor pressure is calculated by the formula

$$\frac{V - V_0}{V} P_t = P \quad (13)$$

where V_0 is the volume of gas initially taken,
 V is the final volume, measured at same temperature and pressure as the initial volume,
 P_t is the total pressure on the gas-liquid system, and
 P is the vapor pressure of the liquid.

This method is inherently less accurate than the others even when all the necessary precautions are taken, unless a single component gas is used to measure the vapor pressure of a one component liquid and the vapor obeys the ideal gas laws, because of errors in the saturation of liquid with gas and in the attainment of equilibrium. Not having any simple exact method for determining the vapor pressure of gasoline, the industry has experimented with a number of more or less empirical tests of no great accuracy.

PREVIOUSLY PROPOSED METHODS

The *I. C. C. or B. of E. method* may be classed as a modified static method. It was designed primarily as a test of shipping

hazard. The apparatus consists of a 2" piece of pipe about 10" long closed on one end and fitted with an opening on the other end which is threaded to take a pressure gauge. The procedure is to fill the bomb entirely full of gasoline, pour out one-tenth of the volume, screw in pressure gauge, heat in water bath at 70° F. for five minutes, unscrew gauge to release pressure, replace gauge, immerse bomb in bath at 90° F. for ten minutes and then read the pressure.

This method has several serious errors, as has been pointed out. Pouring the tenth part of the liquid introduces a variable amount of air into the vapor space. Releasing the pressure at 70° F. causes a loss of some of the lighter constituents of the gasoline. The industry is anxious to replace this method by one more exact.

The *Browne method*¹ is a static method. The apparatus consists of a glass bulb closed at top with a stopcock, through which the sample is drawn and the gas and vapors vented. The bulb is connected at the bottom to a mercury manometer and leveling bottle. A water bath surrounds the bulb for maintaining constant temperature. The vapor pressure of the vented sample is then taken with an arbitrarily chosen vapor space which is kept constant for all readings. The most serious error in this method is that caused by the loss of the lighter constituents in venting and the fact that venting does not completely remove the air.

The *air Equilibrium Method*² is a partial pressure method. Its use has been proposed as a means of determining the vapor pressure of a gasoline on the air free basis. The procedure calls for preliminary saturation of the gasoline by agitating the liquid sample with air. This gas is expelled and a fresh measured portion of air placed in contact with the liquid for making the vapor pressure determination. The rejection of the gases from the preliminary saturation introduces a more or less serious error in the loss of some of the lighter components.

Determinations of vapor pressure by the air equilibrium method were tried because it was receiving serious consideration in research laboratories of some of the oil companies, and because it required little apparatus. The apparatus as constructed in our laboratories consisted of a water bath with glass windows in which a glass bulb of 130 cc. capacity was agitated by means of a shaker driven by the eccentric of a wheel connected to an electric motor. The bulb was closed at top by a stop cock and the bottom was constricted to decrease the chance of any bubbles in the water bath rising through the gasoline. A White³ gas buret and mercury served to measure gas volumes. Since the total pressure on the apparatus was atmospheric plus slight hydrostatic corrections, measurements had to be made at fairly low temperatures in order that the gas volumes would not be extremely large. In these tests run at 15° C. (59° F.) a 50 cc. gasoline sample was used with 10 cc. fresh air sample.

The bulb was filled completely with the sample. Then a 13 cc. vapor space was formed by forcing out liquid with compressed air. The bulb was connected to the shaker and agitated for five hours at 15° C. (59° F.) for preliminary air saturation. At the end of this time the vapor and all but 50 cc. of gasoline were expelled. The bulb was then connected to the gas buret and 10 cc. of air pushed

¹Oberfell and Alden, *Natural Gasoline*, W. B. Conkey Co., Chicago, 1924, p. 99.

²J. Browne, *Am. Chem. Soc.*, 35, 649, 1913. Rhodes and McConnell, *Ind. and Eng. Chemistry*, 15, 1273, 1923.

³G. G. Oberfell, R. C. Alden and H. Hepp, A. P. I. Proceedings of Eighth Annual Meeting, December, 1927, page 106.

⁴White and Campbell, *J. Am. Chem. Soc.*, 27, 734 (1905).

into the bulb. The stopcock on the bulb was closed and agitation started. The temperature was maintained at 15° C. It was expected that after a few hours shaking the gas volume would become constant, denoting equilibrium. Hence, volume measurements were taken every two hours. Unfortunately the volume did not come to a constant value but continued to increase even after eighteen hours of agitation. It was thought that a steady transference of air from water to gasoline took place which continually increased the gas volume. Since this work was done, Oberfell⁴ has reported the same trouble. This method was unsatisfactory in so many ways that work was discontinued on it in favor of other methods which seemed more hopeful.

The Reid Method.—The Reid method⁵ is a modified form of the partial pressure method which proposes to determine the vapor pressure of a gasoline on the air free basis by measuring the increase in total pressure due to the partial pressure of gasoline. This is done by placing above the liquid sample a vapor space three times the size of the liquid sample, with the expected result that the solution or evolution of air will be such a small fraction of the total air present as to have no effect on the partial pressure of the air. The unfortunate part of this scheme is that the large vapor space serves also to vaporize relatively large amounts of the light components, causing an appreciable change in liquid composition with an attendant vapor pressure lowering. The apparatus is made in two parts which are screwed together. The lower part contains the liquid sample while the upper part, which is three times as large and has a pressure gauge attached, is full of gasoline-free air. The two parts are assembled and the whole agitated at constant temperature until the total pressure becomes constant. The partial pressure of the gasoline is then calculated by subtracting the partial pressure of the air from the total pressure. This computation is made by means of the formula:

$$P = P_G - P_a \frac{460 + T}{460 + t} + P_a \quad (14)$$

where P = absolute vapor pressure of gasoline
 P_G = pressure read on gauge
 P_a = atmospheric pressure
 T = temp. in °F. of determination
 t = original temperature in °F. of air in vapor space of the bomb.

The Anderson Method.—The Anderson method¹ is a form of the static method devised as an improvement on the I. C. C. or B. of E. method in which the pouring of the liquid out of the bomb was eliminated. The apparatus consists of a bomb fitted with an opening at the top which is threaded to receive a pressure gauge and an opening at the bottom closed with a valve. The apparatus is first filled with liquid. Then one-tenth of the liquid is withdrawn through the bottom opening. The major objections to this method are that no correction for dissolved air is made and the vapor space changes with temperature due to the expansion of the liquid.

The Davis Method.—The Davis method² is a static method combining an attempt to apply a mathematical treatment to the data in order to obtain the partial pressure of the liquid, corre-

ponding to the vapor pressure of the air free sample. The apparatus is a metal cylinder connected on the side near the bottom to a gauge glass which runs up the side of the metal cylinder but is sealed off at the top. The top of the metal cylinder is fitted with a valve, a pressure gauge, a plugged opening, and an air pump. The hole is unplugged to fill the apparatus and the plug replaced when it is filled to a level at the bottom of the hole. The sample is then heated and vented out the top five times. After this operation the apparatus is tilted until a meniscus shows in the gauge glass. The pressure (P_1) is then read. The hand pump is next operated to reduce the vapor space in the gauge glass to half its first volume. The pressure is again read as (P_2). The contention is that the same amount of air is present in the gauge glass during both readings, and, since it occupied only half the first volume, it had twice the partial pressure at the second reading. As the vapor pressure of the air free gasoline is assumed constant, two simultaneous equations will determine its value.

$$P_1 = P + p_{\text{pair}} \quad (15)$$

$$P_2 = P + 2 p_{\text{pair}} \quad (16)$$

where P = vapor pressure of air free liquid

p_{pair} = partial pressure of air in gauge glass at first reading

$$\dots P = 2P_1 - P_2 \quad (17)$$

This method introduces large errors in venting, in assuming constant quantity of air present in the vapor phase and in the weathering occurring during the filling of the bomb which must be done by pouring. It also magnifies the spring gauge error by multiplying the gauge reading (P_1) by two. The manipulation of this bomb is inconvenient and generally unsatisfactory.

The Beistle-Prather Method.—The Beistle-Prather method³, also a static method, is a combination of the Anderson apparatus and the mathematical treatment of Davis. The apparatus consists of a metal cylinder 2 inches in diameter and about 10 inches long (550 cc capacity) fitted with a gauge glass which shows the liquid level in the apparatus. The top of the bomb is fitted with a threaded opening to receive a pressure gauge and a small pipe running parallel to the cylinder is connected in the side near the bottom and closed with a valve. The bomb is filled by removing the pressure gauge and allowing the gasoline to flow in through the pipe or poured in from the top. When the bomb is full the gauge is replaced, the valve closed and the bomb heated to the desired temperature. Gasoline is now removed by opening the valve and allowing the pressure in the bomb to force it out, or, in the case of too low a pressure, by applying a suction until a 200-cc. vapor space is indicated on the gauge glass. The apparatus is then shaken at constant temperature until constant pressure (P_2) is obtained. Liquid is now removed until a 400-cc. vapor space is indicated. The apparatus is again shaken at the same temperature and the constant pressure (P_1) read on the gauge. As the same theory is applied as was done in the Davis method, the vapor pressure (P) equals $2P_1 - P_2$. This method accomplishes practically the same result as the Davis method without venting and with a simpler procedure. However, it is fundamentally the same and hence open to the same criticisms.

Oberfell⁴ has recently constructed an all glass apparatus to employ the same principle but it allows more accurate volume

³Beistle-Prather, Bureau of Explosives Bulletin, 1926.

⁴Oberfell, Alden and Hepp, *National Petr. News*, Vol. 20, No. 20, May 16, 1928, p. 57.

⁴G. G. Oberfell, R. C. Alden and H. Hepp, A. P. I. Proceedings of Eighth Annual Meeting, December, 1927.

⁵Reid, Vapor Pressure Committee, A. P. I., 1926.

¹Oberfell and Alden, *Natural Gasoline*, W. B. Conkey Co., Chicago, 1924, p. 100.

²H. S. Davis, *Ind. and Eng. Chem.*, 17, 1136 (1925).

measurements and uses a mercury manometer which eliminates the error of the spring gauge.

TESTS FOR GAS-LOCK

At the time that this research was started there was a need for a physical test which would serve to denote the gassing or vapor-locking tendency of fuels. Since the vaporizing of the fuel is closely connected with its vapor pressure, it was believed that such a measurement would prove the best criterion.

The Beistle-Prather Method.—The Beistle-Prather method has many points in its favor. For this reason, an attempt was made to correlate the Beistle vapor pressures with the tendency of a motor fuel to vapor-lock in carburetors.

The first apparatus was made of 2-inch iron pipe and pipe caps. The bomb was 11½ inches long and held 603 cc. of liquid. The only available gauge was a 3-inch test gauge divided in pounds per square inch reading .0 to 30 pounds gauge. The bottom outlet was closed with a ¼-inch Crane needle valve. Although many satisfactory results were obtained with this apparatus, a compound gauge, graduated in quarter-pounds per square inch from zero to 45 pounds per square inch absolute, increased its usefulness by allowing pressures less than atmospheric to be read. Temperature was read on a calibrated mercury thermometer divided in 0.1° Centigrade. A water bath fitted with a coil through which city water, steam and refrigerated brine might be circulated for temperature control, and agitated with compressed air served to maintain the temperature.

The ordinary ¼-inch brass needle valve was found to be too poorly made to stand 40 pounds square inch absolute pressure. The iron construction was too heavy when continued use was made of the apparatus since the necessary agitation was accomplished by shaking the whole bomb. The unscrewing of the gauge was bothersome, made filling of the bomb a sloppy procedure, and was hard on the gauge.

A new bomb (Fig. 25) of 500 cc. capacity, made of all brass construction, using "Hoke" needle valves, and placing a valved outlet just below the gauge thus making it unnecessary to unscrew the gauge, eliminated these objections. The main advantage of this construction is the ease and accuracy of sampling.

In *filling the bomb*, air is displaced, but during this procedure, the sample also weathers some. Therefore, the only way to be sure that the sample taken is identical with the original liquid is to allow considerable of the gasoline to flow through the bomb. Six or seven hundred cc. are considered sufficient to flush the bomb. The sampling is accomplished most easily if the gasoline is under pressure, but when in an open drum, a siphon is arranged so that sufficient pressure is obtained to fill the bomb as before. The sampling of very volatile fuels which are usually kept cold and under pressure requires more careful technique, for as soon as the outlet valve of the container is cracked the gasoline begins to vaporize. In this case the bomb is cooled at least as cold as the sample and maintained so during sampling. The bomb is then connected in the usual way by means of a pipe coupling or rubber tubing depending upon the pressure expected, the valve on the outlet pipe opened, the valve under the gauge tightly closed, and then the valve to the container opened full. When the bomb has acquired the pressure of the container, the valve under the gauge is opened slightly. In this manner the gasoline in the bomb is under practically the same pressure and temperature as the container. The rate with which the bomb can be filled is dependent upon the fuel, its pressure, and temperature. The valve under the gauge can be set to allow only a small trickle of liquid to pass through unattend-

ed thus not wasting the operator's time. When sampling is complete, the valves are closed and the bomb placed in the water bath.

A vapor pressure determination is made according to the following procedure: Temperature is regulated to the lowest value at which vapor pressure is desired. Liquid is then extracted through side pipe until a 200-cc. vapor space is formed. The bomb is then shaken in the water bath until a constant pressure reading is ob-

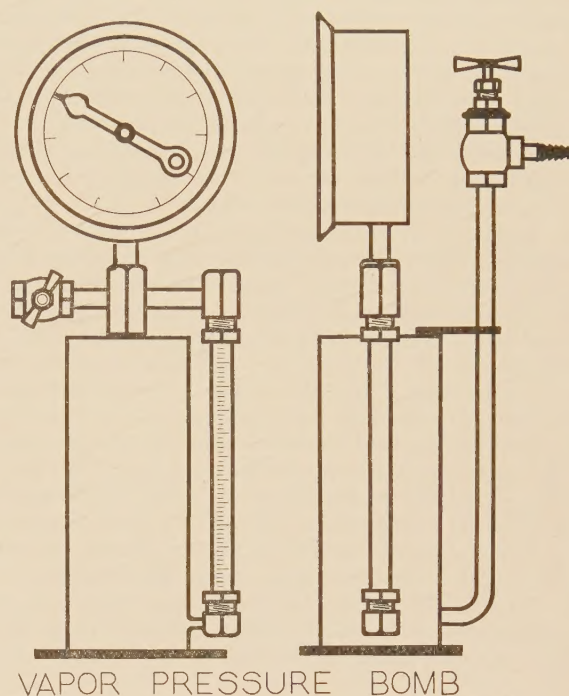


FIG. 25.—Modified Beistle-Prather vapor pressure bomb

tained. After this pressure is read the bath is heated to the next temperature. The rise in temperature causes an expansion of the liquid with a decrease in vapor space. Therefore, additional liquid is removed at the second temperature to again provide a 200-cc. vapor space. The bomb is shaken until a constant pressure is obtained. The temperature is then raised, and the procedure repeated for as many temperatures as desired.

When all temperatures have been covered at the 200-cc. vapor space, the temperature of the bath is brought back to the lowest temperature. Liquid is extracted to form a 400-cc. vapor space and the same procedure followed as given for the 200-cc. vapor space.

Ebullition Test.—The so-called "ebullition test," an apparently simple test that was being used by some laboratories as an indication of the lowest temperature at which vapor formation would occur in a body of liquid open to the atmosphere, was also investigated. As there was no published account of such a test, several modifications of the idea were tried.

The first apparatus consisted of a test tube 1 inch in diameter and 6 inches long, half immersed in a water bath consisting of a 600-cc. beaker. A cover was fitted over the beaker, and the test tube put through a hole in the cover. In making a test cold water (15° C. or 59° F.) was placed in the beaker, 25 cc. or 50 cc. sample of gasoline poured into the cooled test tube, a thermometer placed in the test tube with the bulb in the liquid and held in this position by a slotted cork fitted in the neck of the test tube. The

bath temperature was raised at a rate of 2°C . (3.6°F .) per minute. The ebullition point was taken to be that temperature at which ebullition began and continued to take place as the temperature arose. The results were very erratic, differing by as much as 20°C . (36°F .) on successive tests under the same conditions. These discrepancies are due to the fact that the test conditions are far from equilibrium and the superheating is irregular even on the same sample.

It was thought that the addition of a few grains of clean Ottawa sand would cause less superheating and hence better concordance. This, however, proved otherwise. With the sand present, which was thoroughly wet with the sample before immersing in test tube, there was a tendency to liberate single bubbles of vapor at much lower temperatures than without the sand present. The bubbles occurred with no regularity and no well defined ebullition point was discernible. An increase of the heating rate to 5°C . (9°F .) per minute had no beneficial effect.

A modification of the first apparatus was made in order to reduce the weathering during a test and thus help produce a definite ebullition point. To this end a 50-cc. Pyrex distilling flask with the side arm sealed off was employed with the same thermometer and water bath. In this case a 55-cc. sample was taken which just filled the flask to the neck, leaving a very small surface exposed. Again the same rates of heating were used with and without sand but the deviations between successive trials were 5° to 10°C . (9° to 18°F .) and often no definite value at all would be obtained.

It was not uncommon to get a small evolution of gas at a low temperature and then none until 15°C . (27°F .) higher and then maybe occasional bubbles from there on up. From these considerations it seems that the hydrocarbons superheat to a considerable degree which is dependent upon factors too illusive to be controlled. The results of this investigation were entirely negative. In correspondence with a California oil company it was learned that they also were unable to obtain satisfactory results with this test.

DISCUSSION

All of the methods for determining vapor pressure outlined are subject to a more or less serious error due to changes in composition of the gasoline caused by partial vaporization during the test. In order to obtain a vapor pressure measurement from a liquid sample it is necessary to produce a vapor phase in equilibrium with the liquid and this immediately causes a change in the liquid composition. As may be shown by the phase rule, a binary mixture has one more degree of freedom than a pure substance, therefore, any complex system is not defined until the composition of the liquid is defined. Each time the amount (weight) of vapor formed from a given sample is changed, a new system must be defined which has a different liquid composition and a different vapor pressure. The result is that a vapor pressure measurement of a complex mixture is never taken on the original liquid but on a liquid which differs in composition, depending on the weight of vapor formed, and the temperature.

Equilibrium between vapor and liquid is essential for the accurate measurement on single substances as well as mixtures but the ease of attainment of equilibrium is less for a mixture because the whole body of liquid must be brought into contact with the vapor continually until equilibrium is reached. This makes agitation of the utmost importance in determining the vapor pressure of mixtures.

Another error which is especially bothersome in gasolines is the presence of dissolved gases. By "gas" is meant a compound whose critical temperature is less than the temperature of test. This definition makes oxygen, nitrogen, and methane gases in all

ordinary tests and ethane a gas at all temperatures above 33°C . (90°F .) Although relatively small amounts of these gases have an important influence on the vapor pressure, they have little if any effect on handling losses and vapor-locking tendencies. For this reason it is desired to obtain a vapor pressure reading due only to the liquid hydrocarbons, that is, propane and the higher boiling compounds. It was with this object that the later methods of vapor pressure measurement on gasolines have been devised.

Laboratory measurements on binary mixtures, although simpler than the complex systems represented by natural gasolines are subject to changes in composition upon partial vaporization. The dynamical method was used on binary mixtures by Leslie and Carr.¹ Although carefully conducted, this work has been criticised for the large vapor space used above the liquid without any correction for the attendant change in liquid composition. An analysis of the liquid at the time of measuring the vapor pressure would overcome this difficulty.

Calingaert and Hitchcock² using the static method on binary mixtures developed a mathematical treatment by which the liquid and vapor composition can be determined. Although exact for binary mixtures, it can not be applied to complex mixtures such as gasoline.

Although the methods in use for measuring the vapor pressure of gasolines may be satisfactory for commercial purposes, they are entirely empirical and not founded on a scientific basis. Any accurate method for measuring vapor pressure must

1. Check the vapor pressure of pure single compounds.
2. Give a vapor pressure which can be calculated or interpreted in terms of the compounds present.
3. Give the same vapor pressure regardless of dimensions of apparatus.
4. Check itself on consecutive tests on the same sample.
5. Be so constructed that samples can be placed in apparatus without change in composition.
6. Be constructed to provide for thorough agitation of the sample.

GRADUATED BULB METHOD

Although a fairly satisfactory correlation was found between the temperature at which the Beistle gave atmospheric (740 mm.) pressure and the gassing temperature of the gasoline, it was soon seen that a more accurate method than any of those previously mentioned was needed for a solution of this problem. Therefore, an apparatus was designed and built (Fig. 26) which embodied the features of accurate vapor space and liquid space measurements by means of a graduated bulb, accurate pressure measurement by use of mercury manometer, and positive agitation of liquid and vapor by means of a mechanically operated internal agitator.

The graduated glass bulb which is an important feature of this apparatus forms the end of one side of a mercury manometer. It is in this bulb that the gasoline sample is placed. The bulb is essentially a vertical cylinder fitted at the top with a two-way off-set stop cock, a side arm leaving near the bottom at an angle slightly depressed from 90° to the axis of the cylinder in a vertical direction, and an opening in the bottom shaped to take a stopper. The front of the bulb is etched with volume calibration marks which serve to measure the liquid and vapor spaces and to read the mercury level in the bulb side of the mercury manometer. The top of the bulb is very carefully made so that a minimum dead space or ungraduated space exists from the stopcock to the first graduation mark. This allows the use of very small vapor

¹Leslie and Carr, *Ind. and Eng. Chem.*, 17, 810 (1925).

²Calingaert and Hitchcock, *J. Amer. Chem. Soc.*, 49, 750 (1927).

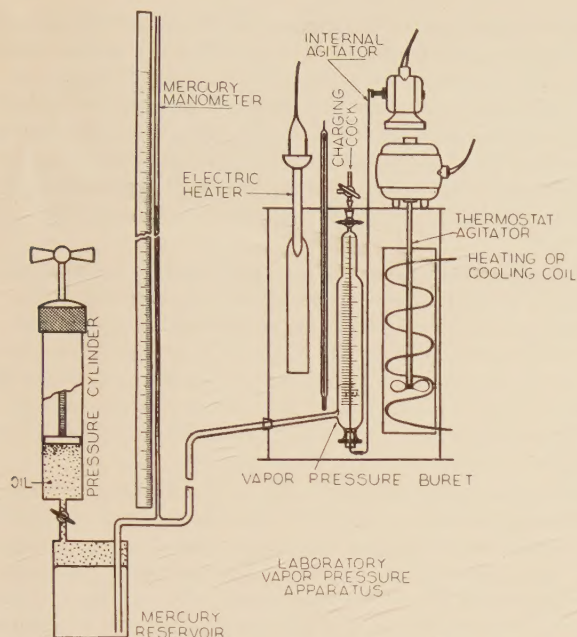


FIG. 26.—Graduated bulb vapor pressure apparatus

spaces. The choice of a stop cock is an important matter for it has to be tight under pressure and vacuum. Although a three-way stop cock would be useful, it is difficult to keep tight under pressure so the simpler two-way capillary offset stop cock was used. With proper precautions this stop cock was tight from 5 mm. of mercury absolute to 2,000 mm. absolute. In order to facilitate filling the bulb a three-way charging cock is connected above the two-way stop cock by a ground glass joint, and except when in use the three-way stopcock is removed.

The side arm near the bottom is the connection to the mercury manometer. It is made on a slant in order to avoid the trapping of air when the mercury is run up into the bulb. This side arm extends through the water bath by means of a flexible connection. Before the flexible connection was devised, considerable trouble was experienced with the breaking off of the side arms. The flexible connection was made by fitting the water bath with a hole through which the side arm was to extend. The hole was tapered to receive a No. 4 rubber stopper from the inside, thus using the hydrostatic pressure to keep it tight. A piece of glass tubing 1 cm. in diameter and just long enough to extend $\frac{1}{2}$ centimeter past the small end of the stopper was put through the stopper at an angle approximately the same as the side arm of the bulb. Over the exposed end of the glass tube was slipped a piece of high grade black gum rubber tubing 2 cm. long. The free end of the rubber tubing contracted down to a small size so that when the stopper, and all, was in place and the side arm of the bulb was put through it, the rubber tubing could be wired down to the side arm and make the water bath tight. This connection was then so flexible that practically no strain was placed on the side arm tending to break it off.

Agitation was obtained by a flattened glass tube which extended up the center of the bulb for its whole length. The flattened part of the stirrer was welded to a round tube just before passing through a good grade rubber stopper which fit in the especially prepared hole in the bottom. After passing through the rubber stopper the tube was bent at right angles to the flat face of the stirrer. A rod was attached to the stirrer by rubber tubing and actuated in a vertical direction by an eccentric run by a motor.

This caused the stirrer to move back and forth using the rubber stopper as a pivot. The intensity of agitation was governed by the speed of the motor. This kind of agitation was very efficient for it caused the vapor to be drawn down into the liquid and broken up into small bubbles. With very fast agitation a veritable froth could be produced. The bottom of the bulb was so tapered that the rubber stopper had a large area of contact. A fairly long stopper was used so that a portion of it extended past the taper and expanded outward forming a tight seat. The stopper was put in with "Duco" Cement and then wired on. Since the stopper was always sealed with mercury no trouble was experienced.

The bulb (23 inches long) was made from a gas buret for the first 10 cc. below the stopcock, where it was joined to a larger tube (2.7 cc. diameter) divided into cc. divisions making a total volume of 105 cc. Twenty-five or fifty cc. samples were used in this with vapor spaces of 0.3 to 50 or 75 cc. A smaller bulb more accurately graduated may be used for small vapor volumes and it requires less mercury.

The glass bulb was submerged on a stand, specially prepared for it, in the water bath to a point just below the stopcock. The water bath was a rectangular copper container 6x7x14 inches high. Two plate glass windows, one front and one back, allowed the bulb to be viewed for readings. In one corner was fitted vertically a metal pumping tube, 2 inches in diameter and 8 inches long, inside of which was wound a copper coil for heating and cooling. The coil was connected to city water, steam, air, and refrigerated brine. A small electric motor mounted directly over the pumping tube was directly connected to a propeller which served to keep the water in circulation in the bath and past the coil. A knife type immersion electrical heater was also in the bath for close control. A mercury and glass thermometer was suspended in the water close to the bulb. Another small motor mounted on a special stand close to the water bath actuated the internal agitator in the bulb. This motor gave a variable speed on the eccentric operating the agitator by means of a variable friction drive. About 200 R. P. M. on the eccentric shaft was generally used.

Pressure measurement was made by a mercury manometer, one side of which was connected to the bulb, the other side was attached to a board on which was mounted three meter sticks vertically above each other. The meter sticks served as the scale for one side of the manometer while the scale on the bulb was calibrated in terms of the meter stick scale and served for measuring the level on the other side of the manometer. The connection between the manometer and the side arm of the bulb was made just outside the water bath with 5 cm. of pressure rubber tubing. The tubing was shellacked inside, allowed to dry, slipped over the joint, wired with three wires on each side, wound with copper wire over the whole length, and heavily shellacked. Winding with wire served to make armored tubing which withstood all pressures with no sign of leaking or failing and shellacking removed the porosity. Instead of the customary leveling bottle connected at the bottom of the U formed by the two sides of the manometer, a hydraulic leveling device was attached. This device consisted of an iron pot serving as a mercury reservoir filled with mercury sufficient for the system, and the balance filled with a thick viscous oil. Two iron tubes enter the top of the reservoir. The tube connected to the manometer extended close to the bottom. The other tube flush with the inside of the reservoir cover connects through a valve to a grease gun or pressure cylinder filled with oil. By this arrangement, the movement of the grease gun piston regulates the flow of mercury into or out of the manometer system. Since the grease gun piston is worked back and forth by the threaded piston rod screwing through a nut, the leveling can be done very accurately.

Sampling.—A vapor pressure measurement can be no more exact than the exactness of sampling. Gasoline being a volatile mixture of hydrocarbons undergoes distillation upon exposure to the atmosphere. The first vapors leaving the liquid are the richest in the light constituents and since these constituents contribute most to the vapor pressure, any vaporization causes a decrease in vapor pressure. This distillation is readily noticed in gasolines having vapor pressures greater than one atmosphere, for when they are exposed vaporization occurs with formation of bubbles. Vaporization losses take place from all gasolines exposed to the air, for the air will contribute a partial pressure equal to the difference between the vapor pressure of the gasoline and the atmospheric pressure. The liquid will then distill with the components exerting their partial pressures as above. Although the process is not so visible, it is still present and causes large errors in sampling.

In order to have the same composition liquid in the vapor pressure apparatus as was in the original container, the liquid should never be poured or otherwise exposed to the atmosphere but should be restrained under such conditions of temperature and pressure during sampling as to exclude the possibility of vaporization. The method adopted for accomplishing this result with the Beistle bomb has already been given. Since the present apparatus is not transportable like the Beistle, a sampler was designed which could sample gasoline from any container and transfer the sample to the vapor pressure apparatus with no change in composition.

The apparatus (Fig. 27) consists in the outer cylindrical container fitted with an outlet at the top (A). Inside and concentric with this container is placed a cylinder open at the bottom but closed at the top except for an exit tube (B) which leads directly outside both cylinders. A tube (C) is run in the side of the outer container near the bottom and bent to extend up close to the top of the inner cylinder. This makes three connections to the sam-

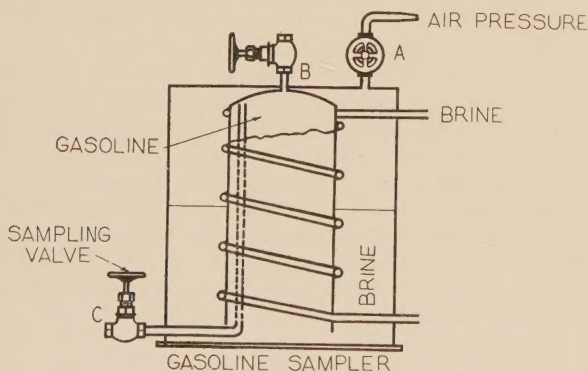


FIG. 27.—Gasoline sampler

pler all of which are valved. A copper spiral coil encircles the outside of the inner cylinder for cooling purposes. The two ends of this coil extend outside the apparatus but are not valved. This apparatus can be made in any size but the one used in conjunction with the vapor pressure apparatus had a cubic capacity of 250 cc. in the inside cylinder and 350 cc. in the annular space between the cylinders.

In sampling gasolines under pressure, about 400 cc. of brine are run into the sampler; cold brine is circulated through the coil to reduce the temperature to about -10°F. ; air pressure is applied at A forcing the brine into the inner cylinder and filling B. C is left closed. B is closed, the air line disconnected and the pressure vented at A. The sampler is then connected to the gasoline container at C. A and B are closed. B is opened slightly as is also C

in order to allow a steady stream of gasoline to run through. This is continued until about 400 cc. of gasoline has passed through. During this operation the pressure in the sampler builds up and compresses the air in the annular space. B is closed and A cracked. When about 200 cc. of gasoline have flowed in, brine will commence to run out at A. A and C are then closed and sampling is complete. If the sample is not to be used immediately, it may be kept indefinitely by running cold brine through the coil and applying a pressure at A.

Procedure.—The vapor pressure apparatus is prepared for the sample by lubricating the stopcock with soft soap and boiling out the trapped air. The boiling out is accomplished by filling the bulb with mercury, closing the stopcock, lowering the mercury to boil out the air, and then raising mercury again to expel the liberated gas. This is repeated until the mercury can be lowered and check the barometer to 5 mm. The three-way stopcock is attached and mercury run up to fill all passages.

The sampler is attached at C to one of the side arms of the charging cock and air pressure applied to the sampler at A. C is opened wide and the charging cock turned to allow the gasoline to run slowly to waste until the cock and lines are cold and cause no vaporizing of sample. Then the charging cock is turned to let the gasoline run into the bulb. Enough gasoline is run in to completely fill the bulb and is then discarded through the charging cock by raising the mercury. Gasoline is again run through the charging cock for a short time to recool the line between sampler and cock. Then gasoline is run into the bulb while the mercury column is so regulated by the pressure cylinder as to keep the greatest possible pressure on the sample. This is continued until the desired volume of gasoline is obtained in the buret. Then the stop cock is closed, C is closed and the sampler and charging cock removed.

Since stop cocks are designed to seal more firmly under vacuum than under pressure, a special procedure is usually necessary to secure tightness under pressure by means of a mercury seal. Mercury is poured in the tube rising from the stopcock and the gasoline in it displaced until a continuous column of mercury rests on the top side of the stopcock key. The mercury in the manometer is lowered until the bulb is under a slightly reduced pressure. The stopcock is turned to allow the mercury thread to run in slowly, and, when a solid column of mercury extends to the end of the capillary inside the bulb, the stopcock is closed. This procedure makes the stopcock mercury sealed against pressure as the mercury thread will remain in the capillary as long as the stopcock is closed. A stout rubber band was wound around the stopcock to act in compression on the key. This served to keep it firmly seated.

To make a vapor pressure measurement the water bath is regulated to the desired temperature, the mercury lowered to form approximately the desired vapor space, and the internal agitator started. Equilibrium is attained when the pressure remains constant. Readings are taken of vapor space, mercury level on manometer scale, mercury level on bulb scale, and temperature. Mercury is withdrawn from the system to form a larger vapor space and the procedure repeated. After obtaining points covering the desired range of vapor space, the temperature is changed and the procedure repeated.

Pressure is calculated by first converting the bulb scale mercury level into manometer scale readings by means of a curve obtained by reading the corresponding levels with the stopcock on the bulb open and the gasoline sample in the bulb. By this procedure all hydrostatic and capillary corrections are avoided. Vapor pressure then equals, barometer, plus manometer side reading, minus bulb side reading, minus temperature correction for mercury corresponding to room temperature. These data result in a curve of

vapor pressure vs. vapor space for each temperature, as shown in Figure 28.

Accuracy.—A test of the accuracy of the entire apparatus was made on a sample of C. P. benzene. An original sample of 18.8 cc. was boiled in the apparatus to remove air until only 5.5 cc. remained. The vapor pressure changed only one millimeter with a change in vapor space from 1.3 cc. to 15.9 cc. The vapor pressure determined on this sample gave 765 mm. Hg. at 80.3° C. and 96 mm. Hg. at 25° C. which checks exactly with the values given by Young. This is taken as an indication of good accuracy.

THEORETICAL CONSIDERATIONS

TRUE VAPOR PRESSURE

In order that a set of vapor pressure data have any significance, it must be based on a constant liquid composition. Hence the vapor pressures of a certain mixture, determined at different temperatures with the same vapor space volume above the liquid, are not comparable for the same vapor space will contain more mols. of vapor as the temperature rises because the vapor pressure of all the compounds concerned rises at a rate greater than the increase in pressure due to the increase in temperature. This means a constantly changing liquid composition. In fact, vapor spaces can not be chosen so that the use of different volumes for each temperature will give a constant liquid composition.

The foregoing leaves only one composition on which to base vapor pressures and that is the composition of the original liquid sample. Since vapor pressures must be determined with a vapor

phase present and since this vapor phase changes the composition of the liquid, it is necessary to determine the vapor pressure at different vapor spaces at the same temperature and extrapolate back to zero vapor volume. The value thus obtained has a definite meaning and the values at all temperatures refer to the same liquid composition.

No vapor pressure method or apparatus previously described embodies the principle of extrapolation of vapor pressure to zero vapor space on the original. The glass bulb was specially constructed to allow the reading of small vapor spaces thus aiding the extrapolation. An example of the data and extrapolation are given in Figure 28. This extrapolation may be accomplished in an approximate manner by extending the general curvature to the zero mark. However, the data from some gasolines give such a steep curve that the extrapolation is uncertain. For this reason

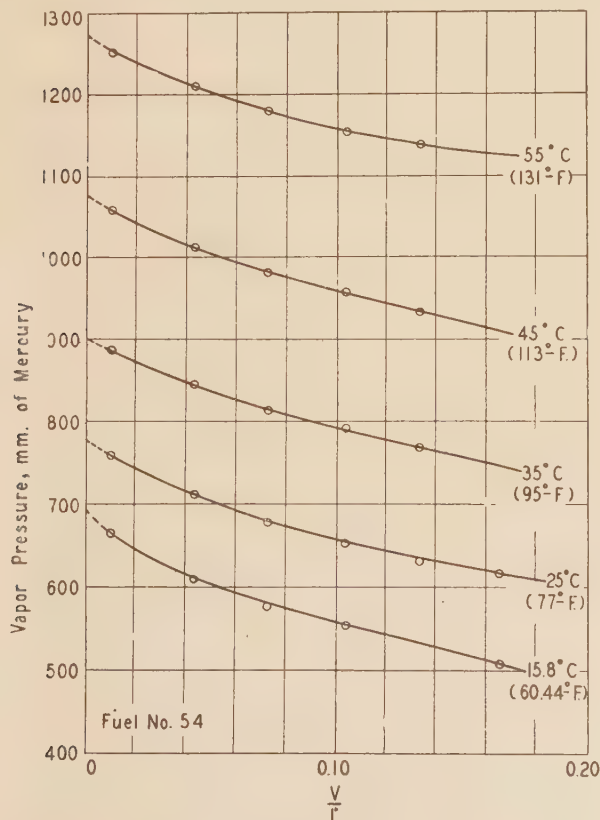


FIG. 28.—Vapor pressure isotherms of Fuel 54 plotted against vapor liquid volume ratio (vapor space divided by liquid volume).

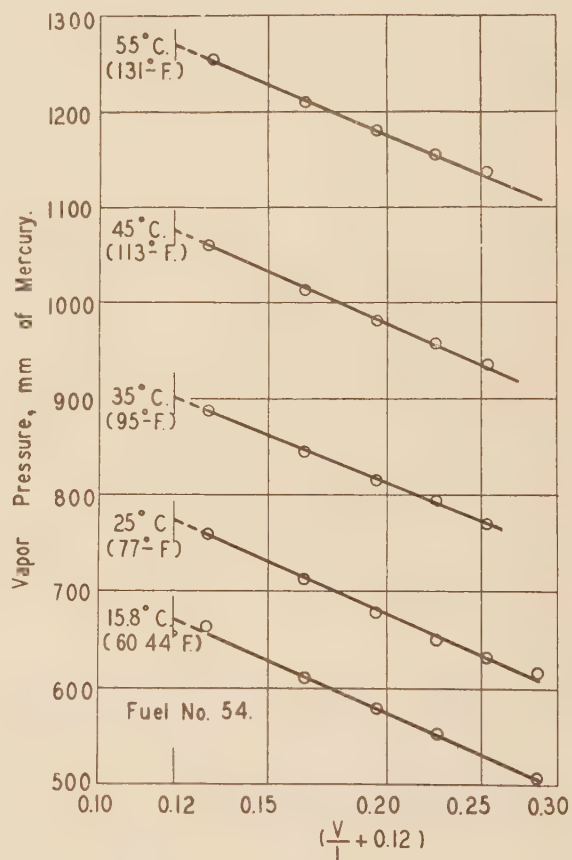


FIG. 29.—Vapor pressure isotherms of Fuel 54 plotted against the log of the sum of vapor-liquid volume ratio plus 0.12, that is, $(\log (\frac{V}{L} + 0.12))$

a more exact method of extrapolating is necessary. A large amount of data were examined¹ and the following equation found to fit in all instances within experimental error up to vapor-liquid volume ratio of 0.7 ($V/L = .7$)

$$\log \left(\frac{V}{L} + 0.12 \right) = aP + b \quad (18)$$

¹T. R. Running, *Empirical Formulas*, John Wiley and Sons, Inc., New York (1917), page 45.

where V = vapor space in cc.
 L = liquid sample in cc. at 25° C.
 a and b = constants
 P = vapor pressure in mm. mercury

This equation (18) indicates that by plotting $\left(\frac{V}{L} + 0.12\right)$

versus P on semi-log paper a straight line results. By extrapolat-

ing to the point where $\left(\frac{V}{L} + 0.12\right) = 0.12$ the vapor pressure at

zero vapor space is obtained as shown in Figure 29. This method serving at once to level the data and extrapolate to zero vapor volume, was checked by comparing the data of Calingaert and Hitchcock² on mixtures of butane and pentane as in Table IX.

These results, as shown in Table IX and Figures 30 and 31, clearly indicate that the vapor pressure extrapolated to zero vapor volume gives the true vapor pressure of the sample originally placed in the apparatus.

GAS-FREE VAPOR PRESSURE

However, it has been suggested that in the case of gasolines, the sample as placed in the apparatus is always contaminated by

TABLE IX

EXTRAPOLATION ON BUTANE-PENTANE SYSTEM

Mol. % Butane in Original Charge of Butane and Pentane	Calingaert and Hitchcock value for V. P. of Liquid of given Composition	Extrapolation on Rectangular Coordinates to Zero Vapor Volume (Figure 30)	Extrapolation on Semi-log Plot to Zero Vapor Volume (Fig. 31)
2.25	556.5	557	558
8.04	633	630	631
12.78	701.6	702	697
19.9	810	825	812.5

dissolved air or other gases, and that the desired vapor pressure is always contaminated by dissolved air or other gases, and that the desired vapor pressure is not that of the original sample but of the so-called "gas-free sample," which we have defined as the vapor pressure of the liquid hydrocarbons including propane and all higher boiling compounds and excluding all compounds of lower boiling points.

Effect of Liquid Composition

The following treatment shows that the vapor pressure of a "gas-free gasoline," containing not more than 7 per cent by weight of propane and 50 per cent of butane varies less than 10 mm. of

mercury as the vapor-liquid volume ratio $\left(\frac{V}{L}\right)$ increases from zero

to one-half. As these percentages may be considered as maximum figures for natural gasoline, the "gas-free" vapor pressure of natural gasolines may be considered a constant independent of vapor volumes not larger than one-half that of the liquid. For motor fuels, aviation fuels, and most natural gasolines the "gas-

²Calingaert and Hitchcock, *J. Am. Chem. Soc.*, 49, 750 (1927).

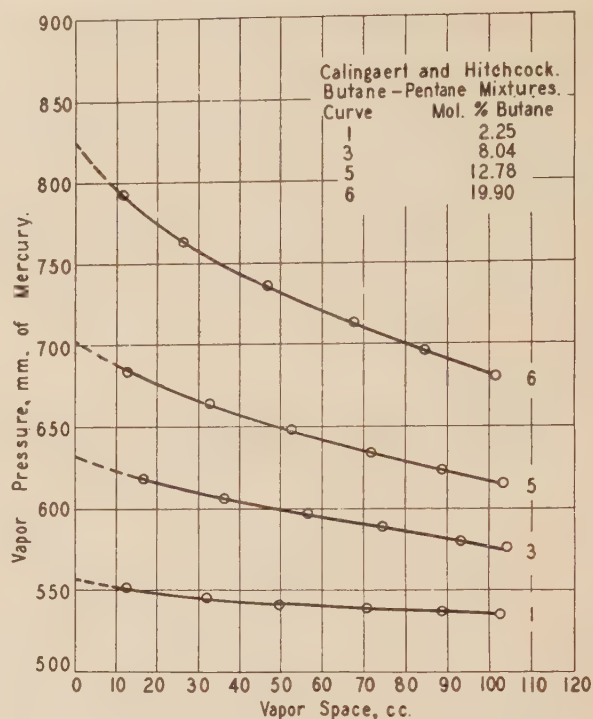


FIG. 30.—Extrapolation of vapor pressure isotherms to zero vapor space, on rectangular coordinates.

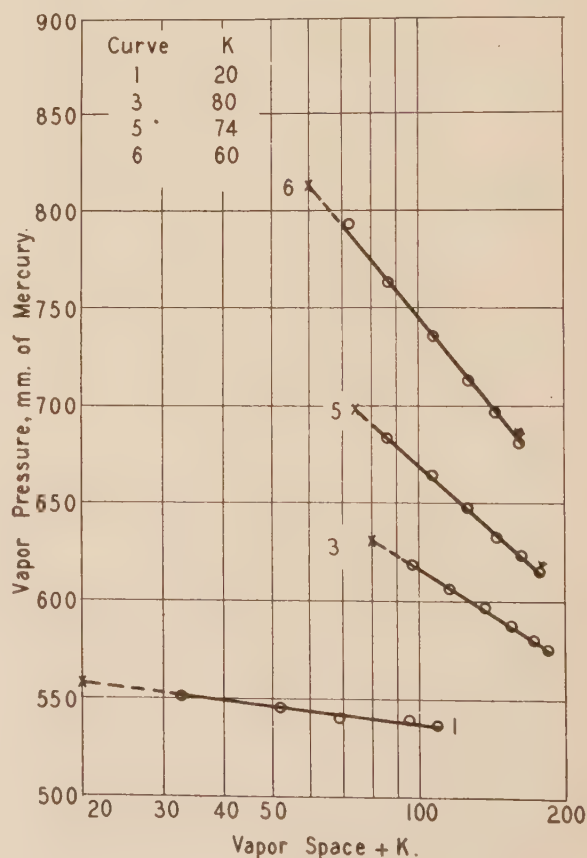


FIG. 31.—Extrapolation of vapor pressure isotherms to zero vapor space on semi-log coordinates.

free" vapor pressure will be constant within 10 mm. of mercury for all vapor liquid volume ratios up to one.

M_A, M_B, M_C = mols. of corresponding component in original sample

P_A, P_B, P_C = vapor pressure of the corresponding pure component in mm. of mercury

m_A, m_B, m_C = mols. of corresponding component in the vapor phase

p_A, p_B, p_C = partial pressure of the corresponding component

V = volume of vapor space in cc.

P = total pressure on the system in mm. of mercury

T = absolute temperature of the system in degrees centigrade

R = gas law constant

Assuming Raoult's Law and the ideal gas laws, which have been shown to apply within the desired accuracy (10 mm.)

$$m_A + m_B + m_C = \frac{PV}{RT} \quad (19)$$

For one mol. of liquid

$$p_A = P_A \frac{M_A - m_A}{1 - \frac{PV}{RT}} \left(\begin{array}{l} \text{partial pressure} \\ \text{of component} \\ \text{A in liquid phase} \end{array} \right) \quad (20)$$

$$p_A = \frac{m_A P}{\frac{PV}{RT}} \left(\begin{array}{l} \text{partial pressure of compon-} \\ \text{ent A in vapor phase} \end{array} \right) \quad (21)$$

Equating 20 and 21 and solving for m_A ,

$$m_A = \frac{M_A P_A}{P_A + \frac{RT}{V} - P} \quad (22)$$

$$\text{likewise } m_B = \frac{M_B P_B}{P_B + \frac{RT}{V} - P}$$

likewise m_C, m_D , etc.

Substitute values of m in equation (19)

$$\frac{M_A P_A}{P_A + \frac{RT}{V} - P} + \frac{M_B P_B}{P_B + \frac{RT}{V} - P} + \dots = \frac{PV}{RT} \quad (23)$$

Rearranging:

$$\frac{M_A P_A}{T + P_A \frac{V}{R} - P \frac{V}{R}} + \frac{M_B P_B}{T + P_B \frac{V}{R} - P \frac{V}{R}} + \frac{M_C P_C}{T + P_C \frac{V}{R} - P \frac{V}{R}} + \dots = \frac{P}{T} \quad (24)$$

Equation 24 may be used to determine P (vapor pressure) as a function of V (vapor volume) but it can be solved only by cut and try methods which may be best accomplished by a graphical method. The description of this method is too long to be included in this year's report but was used in solving equation 24 for the following cases at 25° C. (77° F.):

TABLE X

EFFECT OF VAPOR SPACE ON VAPOR PRESSURE

	Case I		Case II		Case III			Case IV		Case V		Case VI	
	% by Wt.	Mol. Frac.	% by Wt.	Mol. Frac.	% by Wt.	Mol. Frac.		% by Wt.	Mol. Frac.	% by Wt.	Mol. Frac.	% by Wt.	Mol. Frac.
Propane.....	5	0.0811	3	0.0451	1	0.161	Ethane.....	0.076	0.002				
Butane.....	25	0.308	47	0.5371	35	0.4270	Propane.....	1.394	0.025	2.04	0.0345	1.465	0.02505
Pentane.....	25	0.2483	25	0.2303	25	0.2461	Butane.....	11.00	0.15	11.55	0.1489	11.6	0.15035
Hexane.....	35	0.2911	20	0.1543	30	0.2471	Pentane.....	41.53	0.4	38.17	0.3968	38.435	0.4008
Heptane.....	10	0.0715	5	0.0332	9	0.0637	Hexane.....	46.0	0.423	48.24	0.4197	48.5	0.4238
$\frac{V}{L}$	$\frac{P}{mmHg}$		$\frac{P}{mmHg}$		$\frac{P}{mmHg}$		$\frac{V}{L}$	$\frac{P}{mmHg}$		$\frac{P}{mmHg}$		$\frac{P}{mmHg}$	
0.	1306.3		1431.7		1050.9		0	782.35		782.35		720.7	
0.5	1297.3		1425.9				0.5	773.0		776.0		717.9	
1.0	1291.1		1420.5		1044.6		1.0	766.0		773.0		716.0	

The composition used in Case IV is that of a very volatile motor fuel which contains some ethane which is here classified as a gas. The change in vapor pressure with a change in vapor-liquid volume ratio from zero to 0.5 is just within the limits of 10 mm. of mercury. However, if the ethane is removed from such a mixture

and an equivalent amount of propane added to give the same vapor pressure at zero vapor space (Case V), the change in vapor pressure with a change in vapor-liquid volume ratio from zero to 0.5 is about 6 mm. of mercury. The change in vapor pressure is the same in Case V when the vapor-liquid volume ratio changes

from zero to one as it is for Case IV when the vapor-liquid volume ratio changes from zero to 0.5.

The composition given as Case VI is that of Case IV with the ethane removed and vapor pressure calculated for the resulting liquid. This case shows a much smaller change in vapor pressure with change in vapor-liquid volume ratio than either Case IV or V.

Calculations of mixtures containing methane, oxygen, and nitrogen are not made because Henry's law applies to these gases in liquid mixtures at ordinary temperatures, and the proportionality factors in Henry's law are not available for these gases in hydrocarbon mixtures. Their magnitudes estimated by extrapolations of their vapor pressure curves past their critical temperatures would yield a value which is too inaccurate for quantitative work, but from the previous comparisons it can be deduced qualitatively that these gases would cause still larger changes in vapor pressure with changes in vapor-liquid volume ratio.

These comparisons indicate that the compounds classed as gases are responsible for nearly all the change in vapor pressure with change in vapor-liquid volume ratio.

The constancy of the vapor pressure of the "gas-free" liquid was assumed by Davis in his calculations and also adopted by Beistle. However, neither author was concerned with the accuracy of such assumption nor did they calculate allowable limits. The results tabulated in Table X clearly indicate that the Beistle-Prather method commits a larger error than necessary in the use of a vapor-liquid volume ratio of 0.727. The concept of a constant vapor pressure for the "gas-free" liquid can be employed only with due regard to vapor space limits.

EFFECT OF GAS COMPOSITION

Since variable amounts of dissolved methane and ethane probably exist in many gasolines as well as appreciable quantities of air, dissolved from the atmosphere, the change in vapor pressure with changes in the vapor-liquid ratio depends upon the composition of the gas as well as the composition of the gas-free liquid. Therefore, any attempt to attribute the whole change in vapor pressure, even within the limits of a constant "gas-free" vapor pressure, to one gas such as "air" is not strictly true. However, this assumption, which was used by Beistle and Prather, may be justified as an approximation which allows a solution for the "gas-free" vapor pressure.

The assumption of a constant quantity of air in the vapor space above the liquid at all vapor spaces, as made by Davis and Beistle and Prather, is contrary to Henry's law which states that the solubility of a gas in a liquid is proportional to the partial pressure of that gas above the liquid. Hence, the change in partial pressure brought about by a change in vapor space also causes a change in the amount of each gas in the vapor phase.

A *rigorous formula* can be derived which relates total vapor pressure (P), vapor space (V), and vapor pressure of the "gas-free" sample (P_G) by use of Henry's law and the assumption of constant vapor pressure of the "gas-free" sample.

Let X_A, X_B, X_C, X_D = mols. of the corresponding gas dissolved in the liquid at zero vapor space

P_A, P_B, P_C, P_D = partial pressure of the corresponding gas at any vapor space above the liquid

$P_{A_0}, P_{B_0}, P_{C_0}, P_{D_0}$ = partial pressure of the corresponding gas at zero vapor space

P = total pressure on system at any vapor space

P_0 = total pressure on system at zero vapor space

P_G = Vapor pressure of "gas-free" sample

K = proportionality factor between solubility of a gas and its partial pressure

By Henry's law

$$X_A = p_A, K_A \quad (25)$$

$$X_B = p_{B_0} K_B$$

$$X_C = p_{C_0} K_C \quad \text{etc.}$$

at zero vapor space

$$P_0 = P_G + P_{A_0} + P_{B_0} + P_{C_0} + P_{D_0} \quad (26)$$

Let V vapor space be formed

$$P = P_G + P_A + P_B + P_C + P_D \quad (27)$$

$$\text{Mols of gas A vaporized} = \frac{p_A V}{RT}$$

From Equation (25)

$$K_A P_A = X_A - \frac{p_A V}{RT}$$

Rearranging

$$P_A = \frac{X_A TR}{K_A TR + V}$$

Likewise

$$P_B = \frac{X_B TR}{K_B TR + V}$$

$$P_C = \text{etc.}$$

Substitute for P_A, P_B, P_C , etc. in Equation (27)

$$P = P_G + \frac{X_A TR}{K_A TR + V} + \frac{X_B TR}{K_B TR + V} + \frac{X_C TR}{K_C TR + V} + \frac{X_D TR}{K_D TR + V} \quad (28)$$

A knowledge of the constants K_A, K_B, K_C and K_D would allow Equation 15 to be solved by simultaneous equations from five experimental points of vapor pressure versus vapor space. The solution by simultaneous equations would yield P_G , and also the composition of the gas from the values of X_A, X_B, X_C , etc. Unfortunately the numerical values of the constants are not available.

An *approximate formula* can be deduced from Equation (28) if the assumption be made that $K_A = K_B = K_C = K_D$. Then the

denominators in Equation (28) would all be the same and the fractions could be added. Equation (28) would then read:

$$P = P_G + \frac{TR\sum X}{KTR + V} \quad (29)$$

$$\text{or } P = P_G + \frac{c}{a + V} \quad (30)$$

where a and c are constants which depend only on temperature for a given sample.

The assumption made in obtaining Equation (30) amounts to assuming that the effect of all the gases may be treated as one gas. This derivation does not make the assumption of a constant quantity of gas in the vapor space above the liquid at all vapor spaces, as was done by Davis and Beistle, but rather takes into account the change in amount of this gas by an application of Henry's law.

It should be noted that Equation (28) is the true equation for determining the vapor pressure of the "gas-free" sample and that the simplified equation (30) is used only because of the lack of information sufficient to allow Equation (28) to be solved.

A graphical method may be used to test formula (17) for conformity to the data taken by use of the graduated bulb vapor pressure apparatus. Running¹ gives a method for testing data for conformity to Equation (30) whereby a plot of the data should give a straight line. Equation (30) may be rewritten in the form given by Running:

$$P = P_G + \frac{c}{a + V} \quad (30)$$

$$(V + a)(P - P_G) = c \quad (31)$$

If one point, $P_K V_K$, be chosen as correct and values of $P - P_K$

and $V - V_K$ computed, then $\frac{V - V_K}{P - P_K}$ plotted against $V - V_K$

should give a straight line. From this straight line P_G is com-

puted by the relation that the slope of the line equals $-\frac{1}{P_K - P_G}$

The slope is measured and P_K is known so P_G can be computed. Hence, this method of plotting is not only a test for the data but it also gives the desired vapor pressure value.

This has been done in several cases as indicated in Figure 32. As the assumption of constant vapor pressure of the gas free sample holds only for 50 cc. vapor space per mol of liquid, the straight line is drawn through the points for vapor spaces up to 50 cc. per mol.

It is also possible from this plot of the data to compute the number of mols. of gas present in the sample for the intercept of

the straight line on the $\frac{V - V_K}{P - P_K}$ axis equals $-\frac{V_K + a}{P_K - P_G}$. By

measuring the intercept, " a " can be computed. Substituting the value of P_G and " a " in Equation (30) and substituting XTR for c ,

¹Running, T. R., Empirical Formulas, John Wiley and Sons, Inc., New York, 1917, page 53.

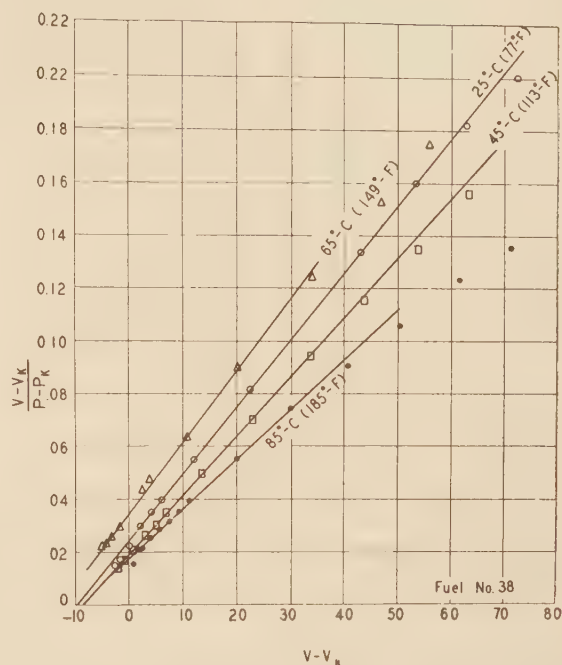


FIG. 32.—Graphical solution of Equation 30 for "gas-free" vapor pressure" Sample 38 at four different temperatures.

the value of X can be computed. For the same sample, the value of X should remain constant for all temperatures. To test this, X was computed at different temperatures on the same sample with results as given in Table XI.

TABLE XI

TEST FOR CONSTANCY OF MOL% OF GAS	
Temp. °C.	X
25	0.0000987
45	0.0000952
65	0.0001097
85	0.0001155

Considering the assumption made in deriving Equation (30) from Equation (28), the check is fairly good.

Although each set of data used to test Equation (30) consisted of five or more points, three points are sufficient for a solution. One point is used as $P_K V_K$ and the other two serve to define the straight line.

A similar graphical test of data calculated by the Davis method as applied to the Beistle-Prather bomb can be made. The Beistle method recommends the use of two vapor spaces 200 and 400 cc. on an original 550 cc. sample but there is nothing in the derivation which forbids the use of any two vapor spaces. In fact, Davis who first proposed the calculation now used by Beistle mentions the use of other vapor spaces. Using the Beistle assumptions and letting

P_1 = total pressure at vapor space 1

P_2 = total pressure at vapor space 2

P_n = total pressure at vapor space V_n

P_1 = partial pressure of air at vapor space 1

Then

$$P_1 = P_G + p_1 \quad (32)$$

$$P_2 = P_G + \frac{V_1}{V_2} p_1 \quad (33)$$

If $V_1 = 200$ and $V_2 = 400$, then

$$P_G = 2P_2 - P_1 \quad (34)$$

but for the general case

$$P_n = P_G + \frac{V_1 P_1}{V_n} \quad (35)$$

$$\text{or } P_n = P_G + \frac{a}{V_n} \quad (36)$$

since $V_1 P_1$ is constant.

Hence, if a set of vapor pressure versus vapor space data at constant temperature be plotted P against $1/V$ a straight line should result whose intercept on the P axis would be P_G . This relation was tested with the data taken in the present apparatus and also with that taken at various vapor spaces in the Beistle bomb.

The plot (Fig. 33) shows a decided curvature so that a line through two points as proposed by Beistle gives a straight line

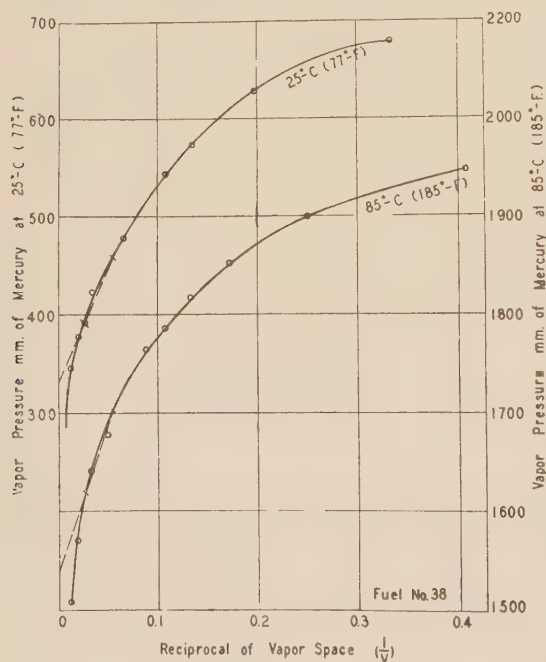


FIG. 33.—Vapor pressure isotherms of Fuel 38 plotted against reciprocal of the vapor space. The Beistle-Prather method assumes these curves to be straight lines as indicated by the dashed lines.

that fits no other two points. Hence, the vapor pressure determined by the Beistle depends entirely upon which two points are used. Since the Beistle vapor pressure is so dependent on the

dimensions of the bomb, it is not a satisfactory vapor pressure method from a scientific standpoint although possibly a satisfactory empirical test.

A comparison of the vapor pressures of different fuels calculated by the Beistle method and by the proposed Graduated Bulb method is given in Table XII. As either method of calculation can be applied to data on either apparatus, the apparatus used is noted after the data.

TABLE XII

COMPARISON OF THE BEISTLE-PRATHER CALCULATED VALUES WITH VALUES CALCULATED BY FORMULA (30)

Beistle Calculation mm. Hg.	Present Method mm. Hg.
861 Graduated Bulb app.	797 Graduated Bulb app.
889 Beistle Bomb app.	797 Graduated Bulb app.
400 Beistle Bomb app.	353 Graduated Bulb app.
1341 Beistle Bomb app.	1260 Graduated Bulb app.
1341 Beistle Bomb app.	1252 Beistle Bomb app.
337 Beistle Bomb app.	306 Graduated Bulb app.
572 Beistle Bomb app.	562 Graduated Bulb app.
955 Beistle Bomb app.	945 Graduated Bulb app.

The proposed calculation always gives a lower vapor pressure than the Beistle. This is believed to be so because the present method comes much closer to giving the vapor pressure of the gas-free sample. The difference is not due to inherent differences in the vapor pressure measured by the different forms of apparatus for it is shown in Table XII that the two methods of calculation applied to the same data yield different answers.

The data of Oberfell, Alden and Hepp¹ gives a comparison of vapor pressure computed by Raoult's Law from analysis of the gasolines for propane and higher boiling compounds, with the vapor pressures computed by the Beistle-Prather method. The data shows that the vapor pressure calculated from analysis are always lower than the Beistle-Prather. An average of the deviations from all data reported, shows the calculated vapor pressure to be 50 mm. of mercury lower than the Beistle-Prather vapor pressure. An average of the data in Table XII shows that the use of equation (30) gives vapor pressure values 54 mm. of mercury lower than the Beistle-Prather computation. This comparison indicates that the results calculated from equation (30) are very close to the vapor pressure of the "gas-free" sample.

The solution of Equation (30) to yield P_G by a graphical method (Fig. 32) useful for leveling a set of data consisting of several corresponding values of total vapor pressure and vapor space, has been indicated. Since only three constants, P_G , c , and a are involved in the solution of equation (30), it may therefore be solved algebraically by the use of only three experimental points.

The algebraic solution:

Let P_1 = total absolute pressure read at vapor space V_1

P_2 = total absolute pressure read at vapor space V_2

P_3 = total absolute pressure read at vapor space V_3

$$P_1 = P_G + \frac{c}{a + V_1} \quad (34)$$

¹Oberfell, Alden and Hepp, *Am. Petr. Inst., Proceedings of Eighth Annual Meeting, December, 1927, pages 120 and 135.*

$$P_2 = P_G + \frac{c}{a + V_2} \quad (35)$$

$$P_3 = P_G + \frac{c}{a + V_3} \quad (36)$$

Rearranging Equation (34)

$$P_1 (a + V_1) = P_G (a + V_1) + c \quad (34A)$$

Rearranging Equation (35)

$$P_2 (a + V_2) = P_G (a + V_2) + c \quad (35A)$$

Subtracting (35A) from (34A)

$$a (P_1 - P_2) + P_1 V_1 - P_2 V_2 = P_G (V_1 - V_2) \quad (37)$$

Rearranging Equation (36)

$$P_3 (a + V_3) = P_G (a + V_3) + c \quad (36A)$$

Subtracting (36A) from (34A)

$$a (P_1 - P_3) + P_1 V_1 - P_3 V_3 = P_G (V_1 - V_3) \quad (38)$$

Multiplying Equation (38) by $(P_1 - P_2)$ and subtracting Equation (37) multiplied by $(P_1 - P_2)$

$$\begin{aligned} & P_1 V_1 (P_2 - P_3) - P_2 V_2 (P_1 - P_3) + P_3 V_3 (P_1 - P_2) \\ & = P_G [(V_1 - V_2) (P_1 - P_3) - (V_1 - V_3) (P_1 - P_2)] \quad (39) \end{aligned}$$

Solved for P_G and rearranging

$$P_G = \frac{P_1 V_1 (P_2 - P_3) + P_2 V_2 (P_3 - P_1) + P_3 V_3 (P_1 - P_2)}{V_1 (P_2 - P_3) + V_2 (P_3 - P_1) + V_3 (P_1 - P_2)} \quad (40)$$

Equation (40) is a general solution of Equation (30) which can be simplified if definite values of V be adopted. For instance, if vapor spaces of 5, 15, and 25 cc. per 50 cc. of original liquid be used, then

$$P_G = \frac{2P_1P_3 - P_1P_2 - P_3P_2}{P_1 - 2P_2 + P_3} \quad (41)$$

Equation (41) has been used to compute the "gas-free" vapor pressure of Fuels 35 and 58 from vapor pressure data obtained by the use of the graduated bulb apparatus. These values are compared in Table XIII with the vapor pressures calculated from the analysis as described in Part VII.

The agreement is excellent in both cases.

VAPOR PRESSURES OF MIXTURES

EFFECT OF TEMPERATURE

The foregoing has been a discussion of vapor pressure vs. vapor space data at constant temperature. The following discussion treats the change in vapor pressure of mixtures with temperature.

It has been assumed by other investigators that mixtures should plot on charts prepared for pure compounds in the same manner as a pure compound, and that this principle may be used as a

test of vapor pressure data of a mixture. However, careful consideration will show that the plot of the vapor pressures of mix-

TABLE XIII

COMPARISON OF "GAS-FREE" VAPOR PRESSURE CALCULATED FROM EQUATION (41) AND VAPOR PRESSURE CALCULATED FROM ANALYSIS

Compound	V. P. mm. Hg. at 60°C (140°F.)	Analysis Fuel 35	Analysis Fuel 58
Propane.....	15900	0.3 Mo. %	0.55 Mol. %
Iso-butane.....	6560	0.56	1.51
Butane.....	4785	4.5	5.22
Iso-pentane.....	2036	5.5	2.82
Pentane.....	1600	9.83	10.19
Iso-hexane.....	807	3.94	2.81
Hexane.....	575	12.93	9.73
Iso-heptane.....	300	9.14	6.18
Heptane.....	210	12.32	20.53
Residue.....	5 (Fuel 35) 10 (Fuel 58)	40.98	40.46

Vapor pressure at 60° C. (140°F.)

Calculated from analysis.....	807 mm. Hg.	732 mm. Hg.
Calculated from Equation 41.....	809 mm. Hg.	735 mm. Hg.

tures may cross each other as well as cross the curves of pure compounds and hence do not follow the same scheme as do the pure compounds.

The following treatment is based on that given by Robinson.¹

Consider a binary mixture of A and B. The vapor pressure of pure A, P_A , can be represented quite accurately over a small temperature range by

$$\log P_A = - \frac{L}{RT} + K \quad (42)$$

Likewise for pure B

$$\log P_B = - \frac{L'}{RT} + C \quad (43)$$

L = molal latent heat of pure A

L' = molal latent heat of pure B

K and C are constants

R = the gas law constant

T = absolute temperature

The assumption of constant latent heats over the small temperature range, which is a frequent assumption in problems of this nature, will allow a possible solution whose qualitative result at least is correct. For some compounds, a constant differing slightly from the latent heat value might be used to better advantage, but if so, the constant would at least be of the same order and vary with the different compounds in the same manner.

Let x = mol fraction of A

y = mol fraction of B

Solving for P_A and P_B in (42) and (43)

¹C. S. Robinson, "Elements of Fractional Distillation," McGraw-Hill Book Company, New York, 1922, page 42.

$$P_A = e^{\left[-\frac{L}{RT} + K\right]} \quad (44)$$

$$P_B = e^{\left[-\frac{L'}{RT} + C\right]} \quad (45)$$

The total pressure (P) by Raoult's Law

$$P = xP_A + yP_B \quad (46)$$

Substitute for P_A and P_B from Equation (44) and (45) into (46)

$$P = xe^{\left[-\frac{L}{RT} + K\right]} + ye^{\left[-\frac{L'}{RT} + C\right]} \quad (47)$$

Equation (47) shows that the total pressure exerted by a liquid mixture does not conform to the same formula as the pure substance for if the logarithm of Equation (47) be taken

$$\log P = e^{\left[xe^{\left[-\frac{L}{RT} + K\right]} + ye^{\left[-\frac{L'}{RT} + C\right]}\right]} \quad (48)$$

The relation is no longer a simple one of $\log P$ versus $\frac{1}{T}$ but a

rather involved relation which would result in a curve on a $\log P$ versus $\frac{1}{T}$ plot. By a double differentiation of formula (35) it can

be shown that the curvature is greatest for the widest boiling range mixture. Hence, the vapor pressure of a gasoline taken at zero vapor space plots with a large curvature whereas the gas free vapor pressure is less curved due to the lower boiling range of the mixture.

A few examples of vapor pressure versus temperature, calculated by Raoult's Law, are shown in Table XIV.

TABLE XIV

A COMPARISON OF THE VAPOR PRESSURE CURVES OF VARIOUS MIXTURES

Temp. °C	Case 1	Case 2	Case 3	Case 4	Case 5
	Hexane	0.5 Hexane 0.5 Octane	0.0941 Octane 0.0059 Propane	0.0795 Propane 0.2 Butane 0.6205	0.1 Propane 0.2 Butane 0.7 Hexane
-40	4	1.7	5	110.9	114.3
0	45	23.57	23.57	537.8	537.8
+50	405	225.0	124.0	2401.6	2318.1

Cases 2 and 3 were calculated to have the same vapor pressure at 0° C. but it is seen that at the other two temperatures the vapor pressures do not coincide. Case 2 has a vapor pressure of 1.7 as against 5 for Case 3 at -40° C. and Case 2 has a vapor pressure of 225 as against 125 for Case 3 at 50° C. Hence, these two mixtures cross each other at 0° C. Case 3 also crosses the curve for

pure hexane given as Case 1. Case 4 and Case 5 each are composed of the same components but their pressure curves cross at 0° C. From these comparisons it is deduced that no general rule can be stated for mixtures and that each mixture has a vapor pressure curve characteristic of its composition and no other composition can reproduce it.

COMPOSITION FROM VAPOR PRESSURE DATA

The foregoing treatment leads to the conclusion that vapor pressure data may be used to compute composition. With a knowledge of the components present, Raoult's and Henry's laws may be applied for this purpose. The components to which Henry's law applies and the corresponding constants are:

O ₂	K _A
N ₂	K _B
CH ₃	K _C
C ₂ H ₅	K _D

The compounds to which Raoult's Law applies and the corresponding vapor pressure of the pure compound are:

Propane.....	P _E
Butane.....	P _F
Isobutane.....	P _H
Pentane.....	P _I
Isopentane.....	P _O
Hexane.....	P _K
Di-iso-propyl.....	P _L
etc.	

Let the mol fraction of each component be represented by X_A, X_B, X_C , etc. At zero vapor space and temperature T_1 , the total vapor pressure, P_1 , is the sum of all partial pressures, or

$$P_1 = \frac{X_A}{K_{A1}} + \frac{X_B}{K_{B1}} + \frac{X_C}{K_{C1}} + \frac{X_D}{K_{D1}} + X_E + P_{E1} + X_F P_{F1} \text{ etc.} \quad (49)$$

Similar equations can be written for as many different temperatures as there are compounds. The resulting equations could be solved simultaneously for all the various x values thus defining the composition.

However, the solution of so many simultaneous equations would necessitate a large amount of calculation which would be simplified by using the "gas free" vapor pressure and from it calculate an "equivalent" composition consisting of

Propane	Hexane
Butane	Heptane
Pentane	

By use of this procedure only five simultaneous equations would result which could be solved handily by use of determinants.

SUMMARY

A critical study of present methods of measuring vapor pressure indicated they are purely empirical and scientifically unsound. A complete discussion of the effect of vapor volume and temperature changes led to the development of an apparatus and method by which the vapor pressure of a gasoline can be accurately determined either "as received" or as "vented" or "gas-free."

The "gas-free" vapor pressure so computed is identical with the vapor pressure computed by Raoult's Law from the fractional distillation analysis of the gasoline for propane and all higher boiling compounds.

The vapor pressure curve of a mixture such as gasoline has been shown to be characteristic of the composition of the gasoline, and a method for determining the composition of a gasoline from its vapor pressure has been indicated.

